JOURNAL OF MATERIALS SCIENCE 23 (1988) 365–370

Phase changes at abraded surfaces of ZrO_2–Sc_2O_3–Al_2O_3 solid electrolyte

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Diamond grinding drastically lowered the surface monoclinic concentration in a ZrO_2–Sc_2O_3–Al_2O_3 solid electrolyte and caused asymmetric broadening of the X-ray diffraction peaks. Annealing in air eliminated the broadening and partly restored the monoclinic concentration, in a manner which suggests that the grinding had converted surface monoclinic to a metastable tetragonal structure.

1. Introduction

Depending on the alloy composition and the external stimuli, the free surfaces of sintered polycrystalline zirconia-based ceramics undergo many interesting transformations. Surface grinding of calcia-partially stabilized zirconia converted tetragonal particles to the monoclinic form [1] and, in an "overaged" alloy, changed some monoclinic to tetragonal [2]. Grinding zirconia–yttria converted surface tetragonal to monoclinic [3] and cubic to tetragonal [4] or to a rhombohedral structure [5]. The latter phase was also found after surface implantation with $^{15}N_2^+$ ions [6]. Grinding tetragonal zirconia–ceria introduced strong preferred orientation at the surface [7]. The as-sintered surface of metastable fully tetragonal zirconia–yttria [8–11] or zirconia–ceria [12] transformed partly or completely to the monoclinic form on annealing at 100 to 500° C in a moist environment, causing a severe deterioration in mechanical properties [13].

In this paper we report changes which occurred at the surface of a ZrO_2–Sc_2O_3–Al_2O_3 material after grinding and on subsequent annealing. The alloy, which is a partially stabilized zirconia containing free alumina, is of technical interest because it is welded as thin discs to alumina tubing to form an industrially useful oxygen sensor [14]. The external surface of the disc is normally ground flat after welding. The work is of more general interest because it supports the grinding-induced conversion of surface monoclinic to a metastable tetragonal structure [2], the opposite reaction to that observed in transformation-toughened zirconia alloys [1].

2. Experimental procedure

Most of these experiments were carried out using discs of composition 50 wt % Al_2O_3, 50 wt % (95.3 mol % ZrO_2 4.7 mol % Sc_2O_3) prepared by blending ZrO_2, Sc_2O_3 and Al_2O_3 powders for 2 h, pressing and sintering for 15 h in air at 1700° C. In some specimens the blending time was varied, in others the Sc_2O_3 was introduced by the precipitation of $Sc(OH)_3$ in the ball mill. Details of the powders used, the blending and precipitation procedures, pressing and sintering have been reported previously [15]. After sintering, the discs were approximately 8 mm diameter and 2 to 3 mm thick.

Three discs prepared from powders blended for 2 h were each ground on one face with a 100 μm diamond wheel. X-ray diffraction was used to identify the phases present before and after grinding, with the 2θ range 27 to 33° (Cu$K\alpha$) being used as described previously [15] to provide data on the proportion of monoclinic at the ground surface. The discs were then annealed in atmospheric air for 1 h at temperatures increasing from 200 to 1700° C in steps of 100° C. The ground surface of each disc was examined by X-ray diffraction as above after each anneal. For comparison, three as-sintered unground discs prepared from the same powder batch were also annealed at identical temperatures and subjected to X-ray diffraction.

If quenched after phase equilibration at the sintering temperature, this material contained α-Al_2O_3, a monoclinic ZrO_2–Sc_2O_3 solid solution of low Sc_2O_3 content and a fluorite-type ZrO_2–Sc_2O_3 solid solution with somewhat more dissolved Sc_2O_3 [16]. The mixed powder route produced a material in which there remained some unreacted or partly reacted zirconia after sintering, caused by inhomogeneities in the initial Sc_2O_3 distribution [15]. Extended milling or the incorporation of Sc_2O_3 by precipitation on the blended ZrO_2 and Al_2O_3 powders improved the Sc_2O_3 dispersion, thereby reducing or eliminating unreacted zirconia [15] and producing a phase mixture closer to that expected from equilibrium considerations [16]. Discs produced by the mixed powder and Sc_2O_3 precipitation routes with milling times from 10 to 10^4 min were examined by X-ray diffraction before and after surface grinding, in order to establish whether the presence of unreacted or partly reacted zirconia

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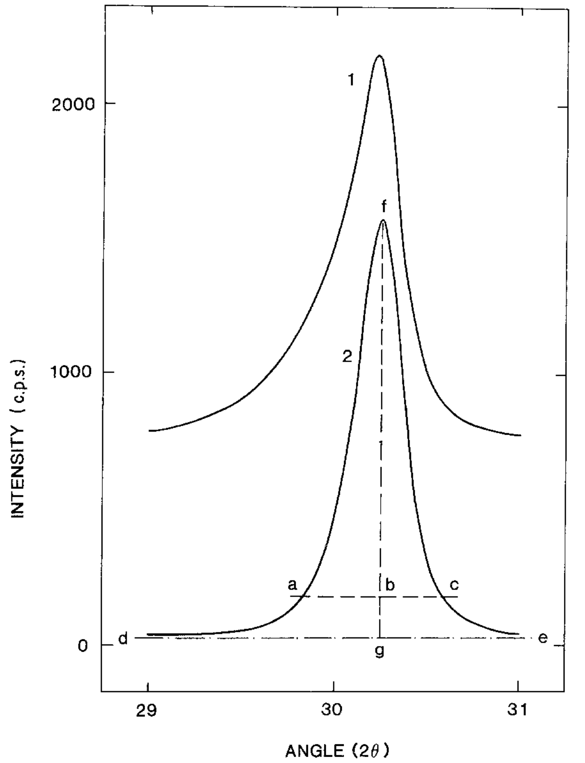

Figure 1 The 1 1 1 cubic peak: (1) ground surface; (2) ground surface annealed 1 h at 700° C in air. To avoid overlap, peak 1 is offset along the intensity axis. The procedure used to characterize the low-angle and high-angle broadening is illustrated on peak 2. Line ac is parallel to the background level de and one-tenth of the maximum intensity fg. Distances ab and bc are measures of the low-angle and high-angle breadths, respectively.

contributed to the phase changes caused by grinding. These discs were not annealed after grinding.

3. Results

3.1. As-sintered surfaces

The as-sintered surfaces gave the X-ray diffraction peaks of α-Al_2O_3, monoclinic ZrO_2 and the fluorite-structure ZrO_2–Sc_2O_3 solid solution. Previous work with a Guinier–Hagg camera on specimens crushed to a powder after long annealing times to achieve thermodynamic equilibrium showed that the solid solution quenched to room temperature was not cubic, but was distorted slightly to the tetragonal form [16]. The resolution of the present low-angle diffractometer traces was inadequate to show tetragonal splitting.

3.2. Line broadening

Grinding caused the cubic peaks to broaden noticeably on the low angle side. Those alumina peaks not affected by overlap (0 1 2, 1 1 0, 1 1 3, 1 1 6) showed similar, but less pronounced, low-angle broadening. A similar effect with ZrO_2–Y_2O_3 was attributed to the formation of a rhombohedral phase at the abraded surface [5]. Discrete rhombohedral reflections, as found after ion bombardment [6], were not observed in the present work.

The asymmetric broadening was progressively eliminated by annealing. Examples of peak shapes are given in Fig. 1. The low-angle broadening decreased steadily as the annealing temperature was increased (Fig. 2a). Grinding also introduced some high-angle broadening, which was only reduced when the annealing temperature exceeded 600° C (Fig. 2b). Annealing at temperatures approaching the sintering temperature completely eliminated the grinding-induced low-angle and high-angle broadening. As might be expected, annealing did not affect the breadth of reflections from the as-sintered specimens. In Figs 2a and b and all subsequent figures the values plotted are the means obtained from three discs and the error bars represent standard deviations.

3.3. Monoclinic concentration

After grinding, the monoclinic peaks were reduced in intensity. The $1\,1\,\bar{1}$ peak was the most severely affected, falling to about one quarter of its initial intensity. The monoclinic concentration, as a volume percentage of the total ZrO_2-based phases present, dropped from 33% in the as-sintered surfaces to 12% in the ground surfaces. A similar decrease for overaged calcia-partially stabilized zirconia was taken to indicate the transformation of some monoclinic back to the tetragonal form [2]. It can be inferred from Fig. 1 of [5] that a reduction in surface monoclinic also occurred when yttria-partially stabilized zirconia was ground. However, Hasegawa [5] commented only that grinding failed to give the expected increase in monoclinic content.

Annealing resulted in a complex pattern of recovery of the monoclinic level (Fig. 3), which showed maxima at 300 to 400° C and at 1300 to 1500° C. Apart from a possible drop at 1700° C, annealing had no significant influence on the surface monoclinic level in the as-sintered specimens.

More information comes from the individual monoclinic peaks. Annealing at up to 1000° C had no effect on the relative area of the monoclinic 1 1 1 reflection; changes in the monoclinic concentration were entirely associated with changes in the relative intensity of the $1\,1\,\bar{1}$ reflection (Fig. 4). Above 1000° C, both peaks were influenced in a similar manner by annealing. Annealing did not change the relative intensities of the individual monoclinic peaks in the as-sintered specimens.

3.4. Effect of preparation technique

The influence of the preparation method is shown in Fig. 5. Adding the Sc_2O_3 by precipitation in the mill resulted in a large grinding-induced decrease in surface monoclinic level which did not depend on the milling time. Using Sc_2O_3 powder gave specimens in which the change in monoclinic level after grinding was lower and which, with increased milling, approached the level shown by the specimens made with precipitated Sc_2O_3.

4. Discussion

4. 1. Monoclinic concentration

Figs 3 and 4 demonstrate that the decrease in surface monoclinic content associated with grinding was not merely a matter of loss by preferred pull-out. The failure of annealing to restore the surface monoclinic form to its as-sintered level suggests that pull-out was responsible for some of the decrease, but the complex pattern of recovery after annealing,

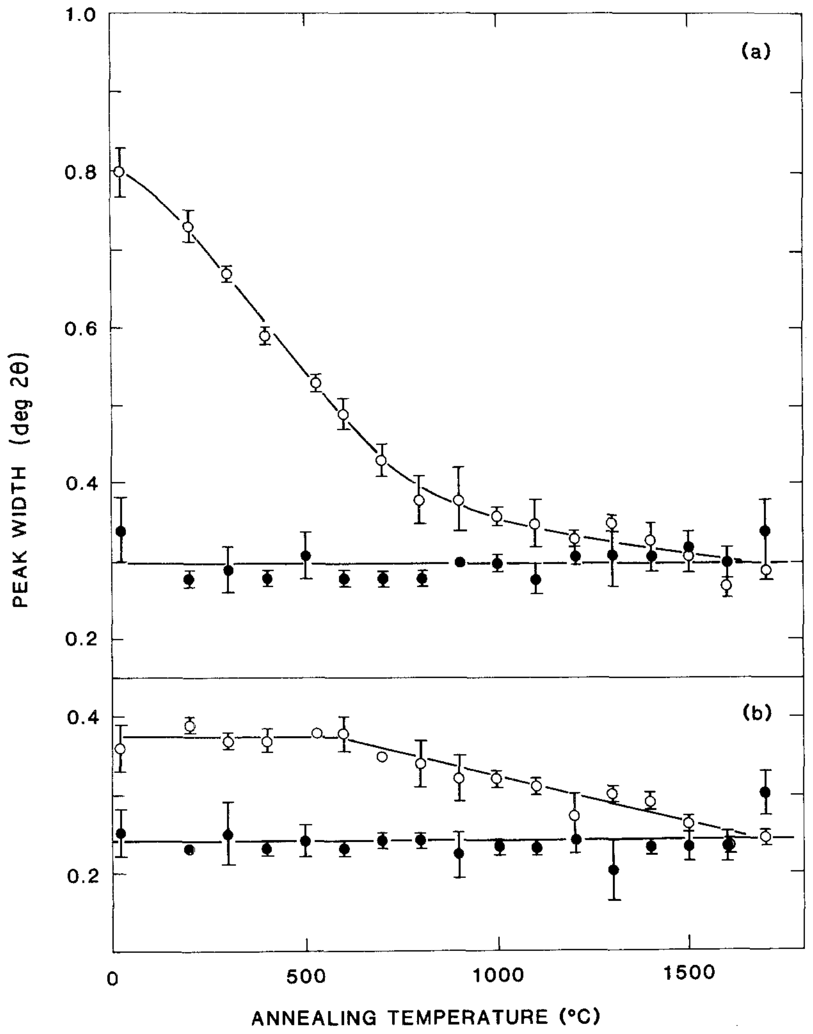

Figure 2 The effect of annealing in air on the one-tenth intensity breadth of the 1 1 1 fluorite X-ray reflection. (a) Low-angle breadth, (b) high-angle breadth. (○) ground surface; (●) as-sintered surface.

particularly below 1000° C, requires additional and more subtle explanation.

The initial recovery of the monoclinic structure, which reached a maximum at 300 to 400° C, occurred at far too low a temperature for it to be associated with solid state precipitation. It is more logical to attribute it to a diffusionless process such as the tetragonal/monoclinic transition. There is a strong similarity between the reappearance of the monoclinic form after low-temperature annealing in this work and the conversion of metastable tetragonal to monoclinic at the surface of as-sintered zirconia–yttria [8–11] and zirconia–ceria [12] on annealing at 100 to 500° C in moist air. In the latter two materials a maximum in conversion was observed at about 200° C. Although not yet demonstrated, the occurrence of a similar reaction for zirconia–scandia seems likely. If moisture is needed to promote the conversion, as is the case with zirconia–yttria [11, 17], it could be provided by the ambient humidity. The absence of any such

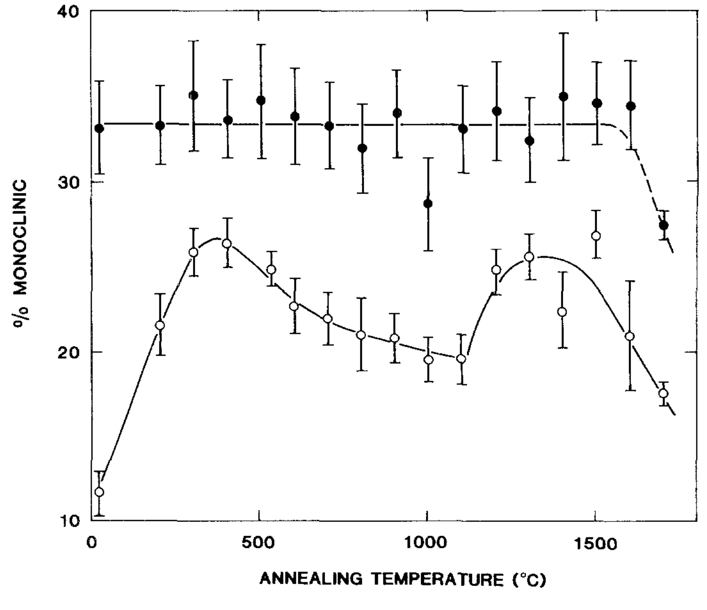

Figure 3 The effect of annealing on the surface monoclinic content. (○) ground surface; (●) as-sintered surface.

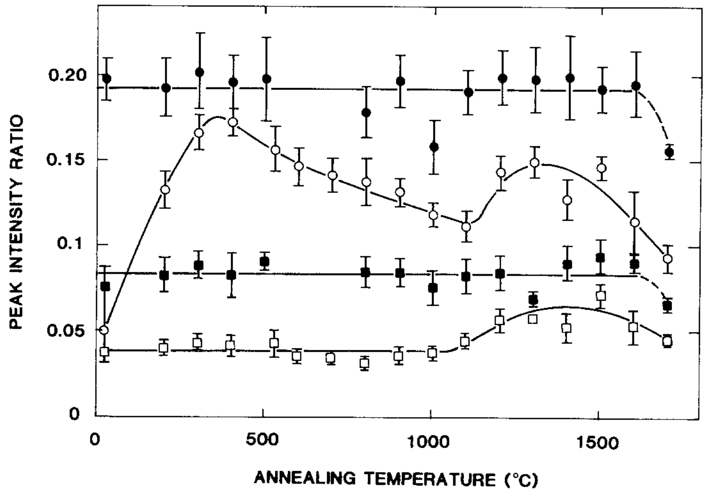

Figure 4 The effect of annealing on the areas of the 1 1 1 and 1 1 $\bar{1}$ monoclinic peaks, as fractions of the total area of the two monoclinic peaks plus the 1 1 1 fluorite peak. (○, ●) 1 1 $\bar{1}$ monoclinic; (□, ■) 1 1 1 monoclinic. (○, □) ground surface; (●, ■) as-sintered surface.

reaction in the as-sintered ZrO_2–Sc_2O_3–Al_2O_3 surfaces suggests that, in the present work, the metastable tetragonal material was generated by the surface grinding. As grinding caused the disappearance of monoclinic, it is probable that the grinding converted surface monoclinic material to particles of a metastable tetragonal phase, as suggested for overaged zirconia–calcia [2].

The major sources of monoclinic in the present materials were unreacted or partly reacted ZrO_2 and a ZrO_2–Sc_2O_3 solid solution which transformed from tetragonal to monoclinic during cooling from the sintering temperature [15, 16]. There may also have been precipitates formed within the fluorite grains during cooling which would have remained tetragonal or changed to monoclinic, depending on their size and composition. The observation that grinding caused more monoclinic to disappear from specimens in which there was no unreacted or partly reacted ZrO_2 (those with Sc_2O_3 added by precipitation or where the powders were given extensive milling) suggests that it was the monoclinic ZrO_2–Sc_2O_3 solid solution which was converted to tetragonal on grinding. This material had a monoclinic/tetragonal transformation temperature well below that of pure ZrO_2.

The lower recovery of monoclinic above 400° C (Figs 3 and 4) occurred for the reason given before [8–12], i.e. the annealing temperature then exceeded the monoclinic/tetragonal transformation temperature of some of the material. In the present case this temperature varied from grain to grain depending on the local Sc_2O_3 concentration and the grain size.

4.2. Surface stresses

Hannink *et al.* [2] attributed the disappearance of monoclinic to "stresses due to grinding". Grinding has been shown to cause substantial biaxial surface compressive stresses in polycrystalline Al_2O_3 [18] and in Al_2O_3–ZrO_2 alloys [19]. Two features of the present work suggest that similar compressive stresses were left in the ground surface. Firstly, the low-angle broadening of the X-ray reflections is consistent with a Poisson increase in interplanar spacing normal to the surface for surface grains. The argument that asymmetric broadening of the cubic peaks indicates a surface rhombohedral phase [5] cannot explain the

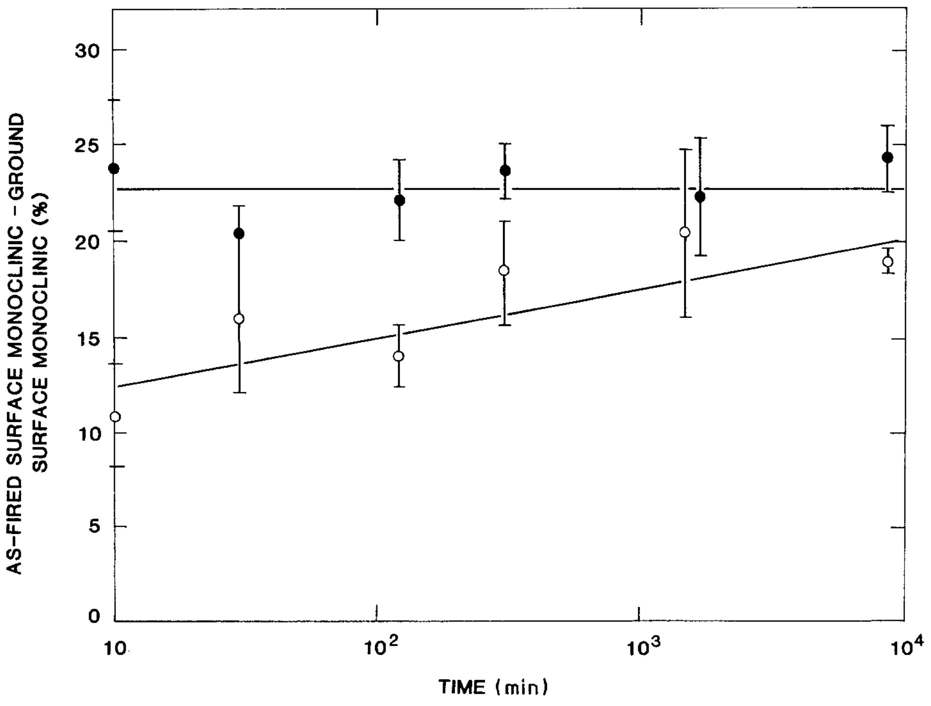

Figure 5 The effect of the method of Sc_2O_3 addition and the milling time on the monoclinic level which disappeared from the surface on grinding. (○) Sc_2O_3 added as powder; (●) Sc_2O_3 added by precipitation.

similar distortion of the α-Al_2O_3 reflections. Secondly, the existence of surface compressive stresses is strongly supported by Fig. 4 which shows that, below 1000° C, the monoclinic phase formed on annealing was material which had $(1\,1\,\bar{1})$ or $(\bar{1}\,1\,1)$ planes parallel to the ground surface. These planes have a separation which is slightly larger than the distance between (1 1 1) planes in the tetragonal structure. Using the cell constants for pure ZrO_2 [20], we calculate that the conversion of tetragonal to monoclinic with $(1\,1\,\bar{1})$ or $(\bar{1}\,1\,1)$ planes parallel to the specimen surface involves a local area contraction at the free surface of about 2%. For ZrO_2–Sc_2O_3 the cell constants are likely to be slightly different but the qualitative effect is the same. The most probable reason for this texture preference during the low temperature recovery of monoclinic is the presence of biaxial compressive stresses in the ground surface. The same texture preference has been reported for the monoclinic phase formed in tetragonal yttria–zirconia ceramics, either by grinding or fracturing [3] or at the compressive surface after creep-rupture testing at 100 to 300° C [21].

The conversion of monoclinic to the metastable tetragonal form on grinding may have resulted from local heating above the transformation temperature combined with surface compressive stresses opposing reconversion to monoclinic. Presumably the reconversion to favourably oriented monoclinic, as observed on subsequent annealing, did not occur because of the very short time spent in the critical temperature range around 300° C. Alternatively, surface compression alone may have been sufficient to convert monoclinic to the tetragonal structure.

4.3. High-temperature annealing

The recovery in monoclinic which occurred above 1100° C seems related to grinding because no such change took place in the as-sintered surfaces. In this region the monoclinic phase showed no pronounced texture, the ratio of the $1\,1\,\bar{1}$ and 1 1 1 peak areas being similar to that observed in the as-sintered specimens. According to the ZrO_2–Sc_2O_3 phase diagram [22], annealing below the sintering temperature should cause a zirconia-rich tetragonal phase to precipitate from the fluorite solid solution. Unless the precipitates were very small, they would change to the monoclinic form on cooling. The observed increase in monoclinic phase at ground surfaces, but not at as-sintered surfaces, suggests that grinding promoted the nucleation and/or growth of precipitates, e.g. by providing dislocations, cracks etc. The persistence of some symmetric line broadening at these temperatures suggests that damage of this kind was present.

The drop in monoclinic content at the highest annealing temperatures, which probably also occurred with the as-sintered samples, is attributable to the re-solution of precipitates in the fluorite solid solution during the anneal. Cooling after annealing was more rapid than after sintering, so less reprecipitation took place.

4.4. Line broadening

Figs 2a and b suggest that two processes contributed to the line broadening and its annealing behaviour. Grinding caused surface damage such as microcracking and the generation of dislocations which, in broadening the peaks symmetrically, was the major contributor to the high-angle broadening. The elimination of this damage required high temperatures, in this case 700 to 1500° C, because processes such as creep were involved. However, the low-angle broadening, which we have attributed to biaxial surface compressive stresses, decreased after annealing at 200° C and had completely disappeared by 800° C. These temperatures were far too low for the stresses to have been relieved by creep. As pointed out earlier, the conversion of metastable tetragonal to monoclinic with $(1\,1\,\bar{1})$ or $(\bar{1}\,1\,1)$ planes parallel to the free surface, which occurred with low-temperature annealing, involved contractions parallel to the surface. This was probably the mechanism responsible for relief of the surface compressive stresses.

5. Conclusions

1. Diamond grinding of a ZrO_2–Sc_2O_3–Al_2O_3 solid electrolyte reduced the surface monoclinic level, broadened the X-ray reflections from α-Al_2O_3 and the fluorite solid solution in a manner suggesting the generation of biaxial surface compressive stresses, and caused general lattice damage.
2. On annealing the ground surfaces in air, there was an initial recovery of the monoclinic phase showing a strong preference for $(1\,1\,\bar{1})$ or $(\bar{1}\,1\,1)$ planes to be oriented parallel to the ground surface.
3. The recovery of monoclinic on annealing at temperatures well below 1000° C suggests that the grinding converted monoclinic ZrO_2 containing a low level of dissolved Sc_2O_3 to a metastable tetragonal form.
4. The texture of the monoclinic form appearing after low-temperature annealing is consistent with the presence of biaxial compressive stresses in the ground surface.
5. Changes which occurred on annealing at temperatures above 1000° C may be explained by normal precipitation processes, enhanced by grinding.

Acknowledgements

Mr I. Bradford assisted with the measurement of surface monoclinic content. The manuscript was reviewed by Mr R. C. Garvie and Drs M. V. Swain and H. G. Scott.

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Received 13 April
and accepted 29 June 1987